Programa de Doctorado
Eletroquímica. Ciencia y Tecnología

PLAN DE INVESTIGACIÓN

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Linea de investigación: Electroquímica del Medi Ambient

Título de la Tesi: Metal-organic frameworks for advanced electro-Fenton treatment of wastewater at near-neutral pH: Preparation of heterogeneous catalysts and enhancement of H_2O_2 production

El projecte ha de constar de les següents parts:
1. Introducción:e interès general del tema
2. Objetivos
3. Plan de trabajo y cronograma
4. Bibliografía

Màxim 1000 paraules (sense comptar la bibliografia)

1. Introduction: Motivation and State-of-the Art

Synthetic chemicals, including pharmaceuticals, dyes, pesticides or industrial additives, are needed for healthcare, agriculture and food production, economic welfare and a wide range of other aspects of modern life. Nonetheless, their worldwide use has caused a gradual accumulation in the water reservoirs [1,2], further entering the food chain [3]. Conventional wastewater treatment technologies are intimately related with the substantial progress in health and environment protection. In spite of this, the diversity and amount of organic pollutants are so vast that water quality has been negatively affected, with conventional treatments becoming less effective to ensure sufficient water decontamination. Within this context, the technologies based on the in-situ promotion of a strong oxidant like the hydroxyl radical ($^{\bullet}OH$) have emerged with a leading role.

In the last decade, the electro-Fenton (EF) process has been intensely explored for the treatment of organic load in wastewater. EF combines two key characteristics [4]: (i) It allows a quick and complete destruction of target pollutants, owing to the massive production of $^{\bullet}OH$ in the bulk solution through Fenton's reaction (1); and, unlike the non-electrochemical Fenton process [5], (ii) the H_2O_2 needed as reactant is generated on site from the O_2 reduction reaction (ORR, (2)) occurring at the cathode surface [6]. As a result, EF is comparatively safer, cheaper and more ecofriendly.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (1)$$
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

Additionally, the anode contributes to the generation of adsorbed hydroxyl radicals from water oxidation and, in the presence of Cl^-, to chlorine production [7]. At present, the main limitation for the deployment of homogeneous EF at a larger scale is its restriction to acidic pH, aimed at preventing the precipitation of the iron catalyst, with the consequent decrease in efficiency [4,5]. This is a serious drawback for the treatment of urban wastewater effluents, which show near-neutral pH.

As an alternative, several materials have been employed as heterogeneous catalysts in EF, including: synthetic iron-loaded structures, such as carbon nanotubes [8], resins [9], zeolites or biosorbents, among others; waste materials like fly ash; zero-valent iron [10]; iron-rich soils like clays [11]; and minerals like iron oxides or pyrite [12]. However, it is unusual that these materials combine a high catalytic activity, stability and recyclability. In general, they suffer from excessive iron leaching, which turns out to be highly detrimental because of the structural modification of the catalyst and the need of time-consuming and costly sludge post-treatment.

Lately, metal-organic frameworks (MOFs) have appeared as potentially superior materials. MOFs are highly ordered and porous crystalline structures synthesized from metal ion/clusters and multidentate organic linkers. They are expected to mitigate some current technical limitations, showing good perspectives for industrial applications [13]. In particular, much interest has been risen for their use in absorption, filtration and degradation of organics in water [14]. Their great appeal arises from their large porosity alongside chemical tunability, which adds to their catalytic nature as recently verified in MOF-catalyzed advanced oxidation processes (AOPs) [15].

The use of Fe-MOFs, either pristine or as precursors of Fe/C hybrids (i.e., MOF derivatives), as catalysts for non-electrochemical Fenton-like process has been recently reported. Some scholars have described the conversion of Fe(III) to Fe(II) active sites [16], which is crucial to maintain the catalytic cycle in solid state. Otherwise, the accumulation of Fe(III) causes the partial destruction of H_2O_2 through the competitive heterogeneous Fenton-like reaction that yields a much weaker oxidant called hydroperoxyl radical:

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+ \qquad (3)$$

Despite the evident advantages of MOFs in model aqueous solutions, their structural instability and other shortcomings have been revealed, thus limiting their scale-up for water treatment. Some researchers have modified the synthesis routes, aiming at obtaining more stable materials. This has led to the fabriction of magnetic and/or photoactive nano/microparticles on carbon, for example. Because of the convenience, economy and high efficiency of magnetic separation, magnetic composite materials have also attracted the attention of environmental protection researchers in the field of adsorption. The application of magnetic MOFs in EF and related process is really incipient, especially in photo-irradiated reactors. Only few works have been published on this topic, being the host group at the UB the first one having launched this research line in 2020. Now, new heterogeneous catalysts for EF process and electrocatalysts for two-electron ORR are needed to operate these water treatments in actual wastewater (at neutral or alkaline pH) using pre-pilot plants.

Copper, as an Earth abundant transition metal, is considered as one of the most important iron-free Fenton-like catalysts [17]. The $^{\bullet}OH$ can be generated from the reaction between H_2O_2 and the Cu(II)/Cu(I) redox species. Note that, unlike iron species, leached Cu^{2+} is predominant as $[Cu(H_2O)_6]^{2+}$ at neutral pH, which presumably favors the operation of Cu-based EF over a wider pH range [18]. Hence, Cu-MOF will be explored as potential heterogeneous catalyst. In addition, this material and/or its pyrolyzed derivatives will be tested in gas-diffusion electrodes (GDE) for H_2O_2 production. Some magnetic/photoactive Fe-based MOFs will be also synthesized to compare their catalytic performance in EF process, whereas other MOF-derived GDEs (for example, based on Co because the group has recently assessed the two-electron route followed by Co-based GDEs) will be characterized and tested. The experiments related to H2O2 electrogeneration and water treatment will be carried out at small scale (150 mL), at pre-pilot scale with filter-press reactors (3 L) in recirculation mode, and in a continous electrochemical reactor.

2. Objectives

The aim of this PhD Thesis is to investigate on the application of MOFs in EF and related wastewater treatments at near-neutral pH from a dual perspective: (i) As heterogeneous catalysts with high activity, stability and performance within a wide pH range, and (ii) as precursors of doped porous carbons further employed to prepare GDEs with high electroactivity for H_2O_2 synthesis. In both cases, the electrolytic trials will be carried out in electrochemical reactors at different scales, with focus on the final implementation of the mentioned materials in a pre-pilot plant operating in recirculation and/or continuous mode.

The synthesis, characterization and applicability of different types of MOFs will be investigated in detail: (1) Magnetic and photoactive Fe-based MOFs will be applied as suspended catalysts in EF process, as well as in photoelectro-Fenton with UVA light or sunlight (PEF and SPEF process, respectively); (2) carbons derived from Cu-MOFs and Co-MOFs will be used to manufacture GDEs that show a higher H_2O_2 production in EF, PEF and SPEF. For comparison, the non-pyrolyzed raw Cu- and Co-MOFs will be assessed as heterogeneous catalysts as well.

These Fe-based, Cu-based and Co-based MOFs will be synthesized via solvothermal route under a range of conditions, trying to identify a correlation between characteristics (morphological, structural, magnetic/photochemical) and performance. The MOF-derived carbons will be obtained under different pyrolysis conditions and then, they will be employed to manufacture the GDEs by spraying the catalyst layer on porous layers. The electroactivity (number of electrons involved in the ORR) of these carbons will be evaluated by rotating disk electrode (RDE) and rotating ring disk-electrode (RRDE) techniques. The viability of the heterogeneous catalysts and GDEs will be assessed in terms of pollutant concentration decay and solution mineralization (i.e., total organic carbon removal). The identification of intermediate compounds and their toxicity will be carried out as well, eventually elucidating the reaction pathways of target organic pollutants (preferentially pharmaceuticals) spiked into the wastewater matrices.

3. Work plan and Schedule

The work plan mainly includes the following tasks:

(1) Getting familiar with the research group, the faculty, and review the state of the art related to the PhD.
(2) Synthesis and characterization of magnetic and photoactive Fe-based MOFs, and their application as suspended catalyst in EF and related processes at lab-scale (150 mL of solution) and larger scale (3 L and/or continuous reactor) with a model organic pollutant and actual wastewater.
(3) Synthesis and characterization of novel (non-Fe)-MOFs (i.e., Cu- and Co-MOFs), and their application as suspended catalysts in EF and related processes at lab-scale (150 mL of solution) with a model organic pollutant. Also, at larger scale if positive results are obtained.
(4) Synthesis and characterization of MOF-derived carbons, manufacture of the corresponding GDEs and testing of these cathodes to produce H_2O_2.
(5) Testing of the new GDEs to treat a model organic pollutant and actual wastewater at different scales.
(6) Simultaneous implementation of the best heterogeneous catalysts and GDEs in EF, PEF and SPEF treatments of wastewater at near-neutral pH at different scales.

In addition, according to 4-year PhD schedule, the following activities are considered:
(7) Short 4-month stay abroad in order to apply for the International Mention.
(8) Attendance to national and international conferences to present oral/poster communications.
(9) Writing and defense of PhD Thesis.

Activity/Term (4 months each)	1	2	3	4	5	6	7	8	9	10	11	12
1. Get familiar with lab, general learning and state-of-the art	X	X										
2. Synthesis, characterization and application of magnetic and photoactive Fe-based MOFs			X	X	X	X	X					
3. Synthesis, characterization and application of novel (non-Fe)-MOFs		X	X	X			X	X	X			
4. MOF-derived carbons, and GDEs (H_2O_2)		X	X	X	X	X						
5. MOF-derived carbons, and GDEs (water treatment)			X	X			X	X	X			
6. Treatment of wastewater at coupling the heterogeneous catalysts and GDEs						X	X	X	X	X		
7. International stay								X				
8. Attendance to conferences		X			X	X		X	X		X	X
9. Writing articles and defense of PhD Thesis			X		X		X		X		X	X

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